

# Band structure of new superconducting AlB<sub>2</sub>-like ternary silicides M(Al<sub>0.5</sub>Si<sub>0.5</sub>)<sub>2</sub> and M(Ga<sub>0.5</sub>Si<sub>0.5</sub>)<sub>2</sub> (M= Ca, Sr and Ba).

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The electronic band structures of the new superconducting (with  $T_C$  up to 7.7K) ternary silicides M(A<sub>0.5</sub>Si<sub>0.5</sub>)<sub>2</sub> (M= Ca, Sr, Ba; A= Al, Ga) in the AlB<sub>2</sub>-type structure have been investigated using the full-potential LMTO method. The calculations showed that the trend in transition temperatures doesn't follow the changes in the density d-states at the Fermi level and probably is associated with phonon-mode frequencies.

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The discovery of superconductivity (SC) in hexagonal AlB<sub>2</sub>-like MgB<sub>2</sub> ( $T_C \sim 39K$ )<sup>1</sup> and creation of promising materials based thereon<sup>2-4</sup> have attracted a great deal of interest in related compounds isostructural with magnesium diboride because of their potential as a new superconductors. One of the remarkable results is the synthesis by a floating zone and a Ar arc melting methods the series of the new ternary layered silicides Sr(Ga<sub>x</sub>Si<sub>1-x</sub>)<sub>2</sub><sup>6</sup>, Ca(Al<sub>0.5</sub>Si<sub>0.5</sub>)<sub>2</sub><sup>7</sup> and (Ca,Sr,Ba)(Ga<sub>x</sub>Si<sub>1-x</sub>)<sub>2</sub><sup>7,8</sup> with transition temperatures  $T_C$  ranging 3.3 - 7.7 K, except for Ba(Al<sub>x</sub>Si<sub>1-x</sub>)<sub>2</sub>. They have the AlB<sub>2</sub>-type structure in which Si and Al,Ga atoms are arranged in honeycomb sheets and alkaline-earth metals are intercalated between them. Furthermore, a series of the compounds (Ca,Sr,Ba)(Al<sub>x</sub>Si<sub>1-x</sub>)<sub>2</sub> were synthesized by varying Al/Si ( $0.6 < x < 1.2$ )<sup>9</sup> and the maximum  $T_C$  for these phases appears at the 1:1:1 composition.

Electrical resistivity and dc magnetization results<sup>5-8</sup> revealed that these layered silicides are a type-II superconductors. The observed different  $T_C$  of these phases would be qualitatively attributed to the change in densities of states at  $E_F$ ,  $N(E_F)$ <sup>8</sup>. The Seebeck coefficient measurements for (Ca,Sr,Ba)(Al<sub>x</sub>Si<sub>1-x</sub>)<sub>2</sub><sup>9</sup> indicate that their carriers are predominantly electrons, in contrast to the holes in magnesium diboride<sup>1-4</sup>.

Recently, the first band structure study of the layered silicides Sr(Ga<sub>x</sub>Si<sub>1-x</sub>)<sub>2</sub>,  $x = 0.375, 0.5, 0.625$  and Ca(Al<sub>0.5</sub>Si<sub>0.5</sub>)<sub>2</sub> has been performed<sup>10</sup>. It has been shown that the SC properties may be due to the high density of (Ca,Sr)d-states at the Fermi level. In the present work we report the results of first-principles calculations for all known 1:1:1 ternary compounds M(A<sub>0.5</sub>Si<sub>0.5</sub>)<sub>2</sub> (M=Ca, Sr, Ba; A=Al, Ga) and analyze the band structure parameters in association of SC properties for the isostructural and isoelectronic compounds: Ca(Al<sub>0.5</sub>Si<sub>0.5</sub>)<sub>2</sub>, Sr(Al<sub>0.5</sub>Si<sub>0.5</sub>)<sub>2</sub>, Ba(Al<sub>0.5</sub>Si<sub>0.5</sub>)<sub>2</sub> and Ca(Ga<sub>0.5</sub>Si<sub>0.5</sub>)<sub>2</sub>, Sr(Ga<sub>0.5</sub>Si<sub>0.5</sub>)<sub>2</sub>, Ba(Ga<sub>0.5</sub>Si<sub>0.5</sub>)<sub>2</sub>. The band structures of the above silicides were calculated by the scalar relativistic full-potential LMTO method<sup>11</sup>. The lattice parameters used are listed in the Table 1.

Energy bands, total and site projected  $\ell$ -decomposed

densities of states (DOS, LDOS) of M(A<sub>0.5</sub>Si<sub>0.5</sub>)<sub>2</sub> are presented in Figs. 1-7. Let us discuss the band structures of M(A<sub>0.5</sub>Si<sub>0.5</sub>)<sub>2</sub> for example Ca(Al<sub>0.5</sub>Si<sub>0.5</sub>)<sub>2</sub>. The valence band (VB) for Ca(Al<sub>0.5</sub>Si<sub>0.5</sub>)<sub>2</sub> includes four fully occupied bands and has a width of about 10 eV. The quasi-core s-like band is located in the interval from 10.0 to 7.8 eV below the Fermi level and separated by a gap ( $\sim 1.45$  eV) from the hybrid (Al,Si)sp-states which form four  $\sigma(2p_{x,y})$  and two  $\pi(p_z)$  bands, Fig. 1. The  $E(k)$  dependence for  $p_{x,y}$  and  $p_z$  bands differs considerably. For  $2p_{x,y}$  like bands the most pronounced dispersion of  $E(k)$  is observed along the direction  $k_{x,y}$  ( $\Gamma$ -K of the Brillouin zone (BZ)). These bands are of the quasi two dimensional (2D) type. They form a quasi-flat zone along  $k_z$  ( $\Gamma$ -A). The (Al,Si) $p_{x,y}$  orbitals participate strong covalent  $\sigma$ -states to form 2D honeycomb network bonds of  $sp^2$  type with the s states. The (Al,Si) $p_z$ -like bands are responsible for weaker  $\pi(p_z)$  interactions. These 3D-type bands have the maximum dispersion in the direction  $k_z$  ( $\Gamma$ -A). The Ca,s,p,d-states are admixed to p-like bands. The  $\sigma(p_{x,y})$  and  $\pi(p_z)$  bands intersect at the  $\Gamma$  point of the BZ. It is important that the (Al,Si)p-bands are located below  $E_F$  and do not contain hole states as well as those in non-superconducting AlB<sub>2</sub><sup>2-4</sup>, which is isoelectronic to the Ca(Al<sub>0.5</sub>Si<sub>0.5</sub>)<sub>2</sub>. The main contribution to the Ca(Al<sub>0.5</sub>Si<sub>0.5</sub>)<sub>2</sub> DOS in the vicinity of the Fermi level is made by the Ca3d-states: their contribution in  $N(E_F)$  is about 59 % compared with 9 % and 10% for Alp- and Sip-states, respectively. Let us compare the band structures of Ca(Al<sub>0.5</sub>Si<sub>0.5</sub>)<sub>2</sub>, Sr(Al<sub>0.5</sub>Si<sub>0.5</sub>)<sub>2</sub> and Ba(Al<sub>0.5</sub>Si<sub>0.5</sub>)<sub>2</sub>. The most obvious consequence of the alkaline-earth metal variation (Ca  $\rightarrow$  Sr  $\rightarrow$  Ba) is the decreasing of VB width from 10.0 (Ca(Al<sub>0.5</sub>Si<sub>0.5</sub>)<sub>2</sub>) to  $\sim 9.1$  eV (Ba(Al<sub>0.5</sub>Si<sub>0.5</sub>)<sub>2</sub>) caused by the increased cell volume. The location and dispersion of lowest d-bands depend from the alkaline-earth metals. As is seen from Fig.1, (Sr,Ba)d-states form the nearly flat bands in the direction L-H, close to  $E_F$ . As a result for Sr(Al<sub>0.5</sub>Si<sub>0.5</sub>)<sub>2</sub>, Ba(Al<sub>0.5</sub>Si<sub>0.5</sub>)<sub>2</sub> the sharp peaks in LDOS of (Sr,Ba)d-states hybridized with (Al,Si)-orbitals, appear which are separated by a pseudogap from the bonding p-bands (Figs. 2-4). The

values of  $N(E_F)$  increases more than twice going from  $\text{Ca}(\text{Al}_{0.5}\text{Si}_{0.5})_2$  to  $\text{Ba}(\text{Al}_{0.5}\text{Si}_{0.5})_2$ . It is important to note that the increase in  $N(E_F)$  is due to simultaneously growth in LDOS of valence states for all atoms in silicates, see Table 1.

The band structures of  $\text{M}(\text{Al}_{0.5}\text{Si}_{0.5})_2$  and  $\text{M}(\text{Ga}_{0.5}\text{Si}_{0.5})_2$  are similar, Fig.1. Their differences are revealed in an increase in the dispersion of  $\sigma$ -,  $\pi$ -bands in the A-L-H directions and a decrease in band gap (at  $\sim 1.0$ - $0.9$  eV) between s- and p-like bands for  $\text{M}(\text{Ga}_{0.5}\text{Si}_{0.5})_2$  compared with  $\text{M}(\text{Al}_{0.5}\text{Si}_{0.5})_2$ . The VB width of  $\text{M}(\text{Ga}_{0.5}\text{Si}_{0.5})_2$  increases by  $\sim 1.3$ - $1.0$  eV. The change of the alkaline-earth metal in the sequence  $\text{Ca} \rightarrow \text{Sr} \rightarrow \text{Ba}$  causes the increase of the  $N(E_F)$ , the M d-states make the main contribution to near-Fermi DOS, Figs. 5-7, Table 1.

Thus, the band structure of the ternary  $\text{AlB}_2$ -like silicides is quite different from SC  $\text{MgB}_2$ . As compared by magnesium diboride, for  $\text{M}(\text{Al}_{0.5}\text{Si}_{0.5})_2$  were found (i) the filling of the bonding  $p_{x,y}$ -bands and the absence of  $\sigma$ -holes, (ii) the increase of covalent interactions (due to p-d-hybridization) between graphene-like (Al,Si) or (Ga,Si) sheets and metal hexagonal layers and (iii) the principal change in the composition of  $N(E_F)$ , where the alkaline-earth metal d-states make the main contributions (55-60 %, Table 1).

According to the experimental data<sup>5-9</sup>: (i) in the silicides  $\text{M}(\text{Al}_{0.5}\text{Si}_{0.5})_2$  the  $T_c$  decreases monotonically when the metal M is changed from Ca to Ba; (ii) in the silicides  $\text{M}(\text{Ga}_{0.5}\text{Si}_{0.5})_2$  the  $T_c$  changes slightly (within range 3.9-5.1) with the maximum (5.1K) for  $\text{Sr}(\text{Ga}_{0.5}\text{Si}_{0.5})_2$ , Table 1.

In framework of BCS theory, the  $T_c$  can be estimated by the McMillan equation  $T_c \approx < \omega > \exp(-\lambda)$ , where  $< \omega >$  is the averaged phonon frequency (inversely proportional to the atomic masses),  $\lambda$  is the electron-phonon coupling constant ( $\lambda = N(E_F) < I^2 > / < M^2 >$ ,  $< I^2 >$  is the electron-phonon matrix element, the value of  $< M^2 >$  does not depend on mass and is determined by force constants).

The values of  $N(E_F)$  (as the contributions in  $N(E_F)$  from Md-, (Si, Al, Ga)p-states) obtained here showed that (i)

in the silicides  $\text{M}(\text{Al}_{0.5}\text{Si}_{0.5})_2$  and  $\text{M}(\text{Ga}_{0.5}\text{Si}_{0.5})_2$   $N(E_F)$  increases monotonically when the alkaline-earth metal is changed from Ca to Ba (it is opposite to  $T_c$  trend<sup>5-9</sup>), (ii)  $N(E_F)$  in the silicides  $\text{M}(\text{Al}_{0.5}\text{Si}_{0.5})_2$  are higher than  $N(E_F)$  in the silicides  $\text{M}(\text{Ga}_{0.5}\text{Si}_{0.5})_2$  based on the same M, what also does not correlate with the observed critical temperatures. Thus, the direct relationship  $T_c \sim N(E_F)$ , suggested in<sup>7</sup> for the "strong stoichiometric" compositions of silicides  $\text{M}(\text{Al}_{0.5}\text{Si}_{0.5})_2$  are impossible.

It may be supposed that the main factor, determining the variation in  $T_c$  in a number of isostructural and isoelectronic compounds  $\text{M}(\text{Al}_{0.5}\text{Si}_{0.5})_2$ , is the change of phonon frequencies depending from the atomic masses. Additionally, the shape of DOS (and the value of  $N(E_F)$ ) may be changed owing to disorder in the distribution of (Al,Ge)/Si atoms in honeycomb layers. As a result alkaline-earth metals will be in different trigonal-prismatic positions, that may lead to the splitting of near-Fermi bands and to a decrease in  $N(E_F)$ . This effect will be more strong for Sr,Ba-containing silicides, where for "ideal ordering" state the  $N(E_F)$  is determined by narrow intensive peaks in DOS, Figs. 3,4,6,7. The possibility of chemical disordering and the inhomogeneity in the arc melted samples of silicides were noted by authors of<sup>7</sup>.

In summary, our calculations of the band structure of all known ternary silicides with the stoichiometry  $\text{M}(\text{Al}_{0.5}\text{Si}_{0.5})_2$  showed that the Fermi level is located in the region of a sharp DOS peak originated mainly from alkaline-earth metal d-states with some contributions of (Al,Ge,Si)p-orbitals. The  $T_c$  behavior for the isostructural and isoelectronic  $\text{M}(\text{Al}_{0.5}\text{Si}_{0.5})_2$  cannot be identified with the variation of  $N(E_F)$ , and probably connected with phonon-mode frequencies determined by atomic masses.

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TABLE I: . The lattice parameters ( $a, \text{\AA}$ ,  $c/a$  [8]), total and site-projected  $\ell$ -decomposed DOSs at the Fermi level ( $N(E_F)$ , states/eV) and transition temperatures ( $T_c$ , K) of silicides  $M(\text{Al}_{0.5}\text{Si}_{0.5})_2$  ( $M=\text{Ca}$ ,  $\text{Sr}$ ,  $\text{Ba}$ ;  $A=\text{Al}$ ,  $\text{Ga}$ ).

Parameters	$\text{Ca}(\text{Al}_{0.5}\text{Si}_{0.5})_2$	$\text{Sr}(\text{Al}_{0.5}\text{Si}_{0.5})_2$	$\text{Ba}(\text{Al}_{0.5}\text{Si}_{0.5})_2$	$\text{Ca}(\text{Ga}_{0.5}\text{Si}_{0.5})_2$	$\text{Sr}(\text{Ga}_{0.5}\text{Si}_{0.5})_2$	$\text{Ba}(\text{Ga}_{0.5}\text{Si}_{0.5})_2$
$a$	4.1905	4.2407	4.2974	4.1201	4.1875	4.2587
$c/a$	1.0498	1.1171	1.1967	1.0777	1.1331	1.1985
M-s	0.028	0.061	0.083	0.017	0.034	0.044
M-p	0.096	0.138	0.199	0.073	0.036	0.076
M-d	0.663	1.344	1.460	0.594	0.936	1.079
M-f	0.0	0.0	0.134	0.0	0.0	0.108
Al(Ga)-s	0.023	0.022	0.018	0.022	0.017	0.017
Al(Ga)-p	0.101	0.345	0.404	0.104	0.162	0.219
Al(Ga)-d	0.033	0.043	0.038	0.015	0.018	0.016
Si-s	0.023	0.013	0.009	0.019	0.014	0.013
Si-p	0.116	0.241	0.237	0.105	0.163	0.164
Si-d	0.044	0.067	0.066	0.042	0.051	0.051
Total	1.127	2.273	2.611	0.992	1.431	1.757
$T_c$ , K	$7.7^6$ $7.8^9$	$4.2^8$	$< 2^{8,9}$	$4.3^7$	$5.1^{8,9}$	$3.9^8$

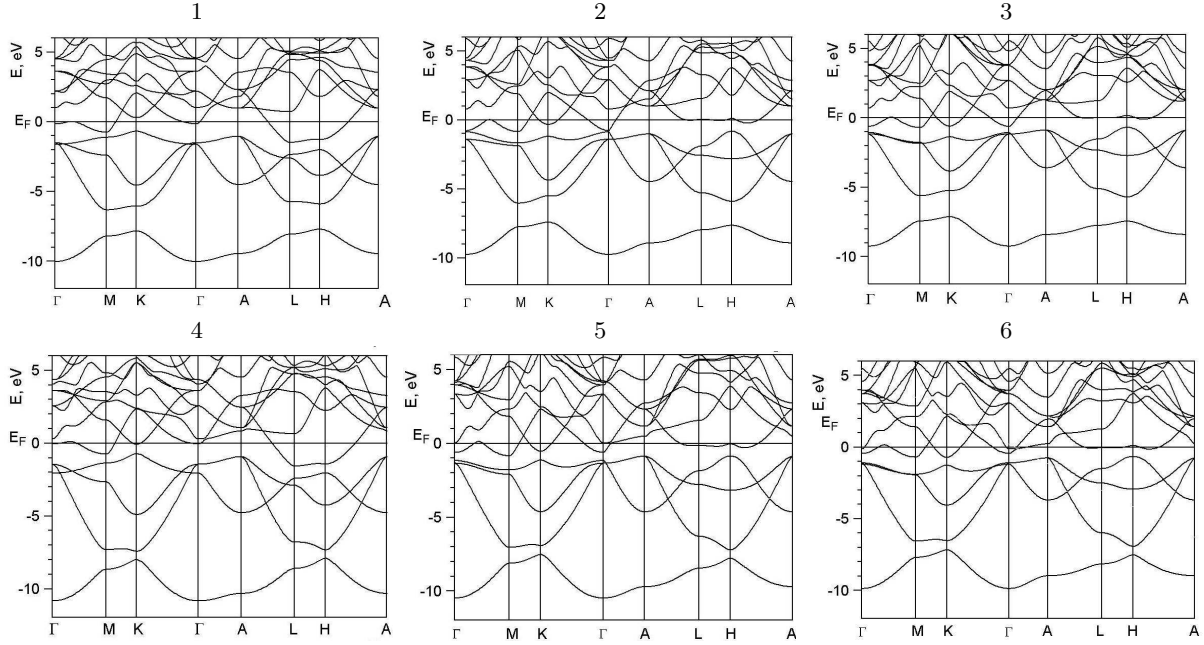


FIG. 1: Energy bands: 1 -  $\text{Ca}(\text{Al}_{0.5}\text{Si}_{0.5})_2$ ; 2 -  $\text{Sr}(\text{Al}_{0.5}\text{Si}_{0.5})_2$ ; 3 -  $\text{Ba}(\text{Al}_{0.5}\text{Si}_{0.5})_2$ ; 4 -  $\text{Ca}(\text{Ga}_{0.5}\text{Si}_{0.5})_2$ ; 5 -  $\text{Sr}(\text{Ga}_{0.5}\text{Si}_{0.5})_2$ ; 6 -  $\text{Ba}(\text{Ga}_{0.5}\text{Si}_{0.5})_2$ .

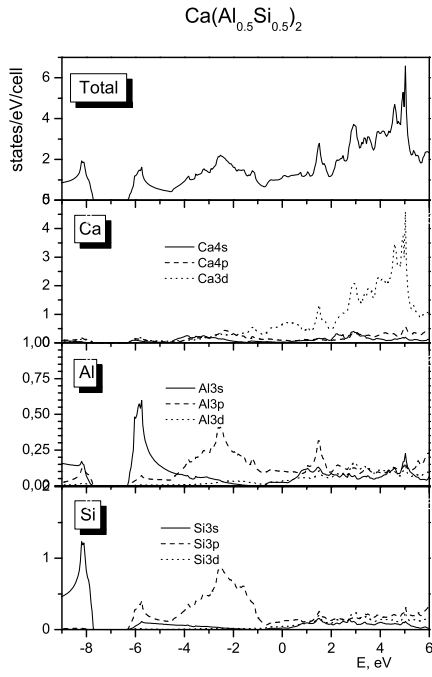


FIG. 2: Total and site-projected  $\ell$ -decomposed DOSs of  $\text{Ca}(\text{Al}_{0.5}\text{Si}_{0.5})_2$ . The energies are relative to the Fermi level.

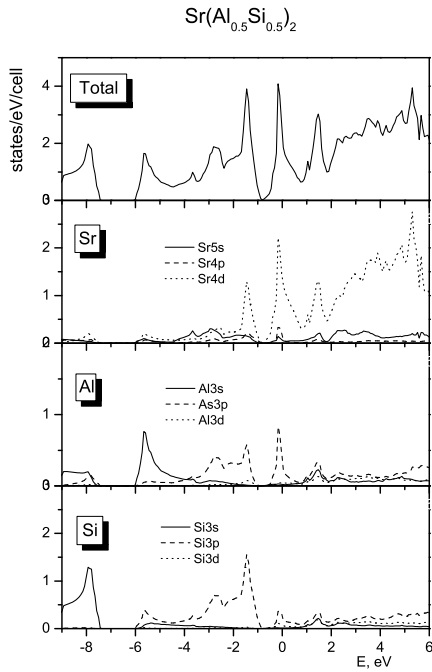


FIG. 3: Total and site-projected  $\ell$ -decomposed DOSs of  $\text{Sr}(\text{Al}_{0.5}\text{Si}_{0.5})_2$ . The energies are relative to the Fermi level.

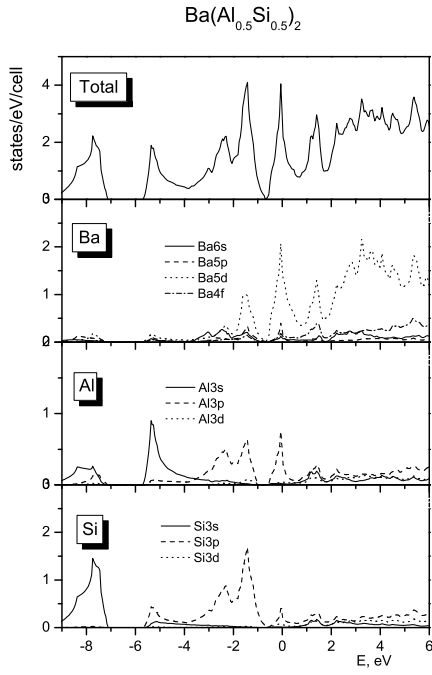


FIG. 4: Total and site-projected  $\ell$ -decomposed DOSs of  $\text{Ba}(\text{Al}_{0.5}\text{Si}_{0.5})_2$ . The energies are relative to the Fermi level.

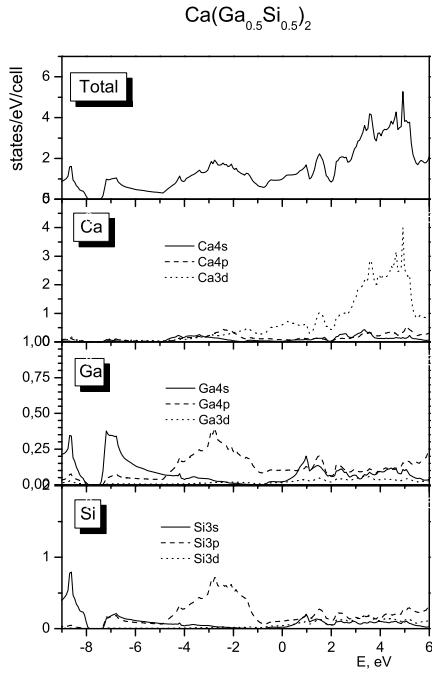


FIG. 5: Total and site-projected  $\ell$ -decomposed DOSs of  $\text{Ca}(\text{Ga}_{0.5}\text{Si}_{0.5})_2$ . The energies are relative to the Fermi level.

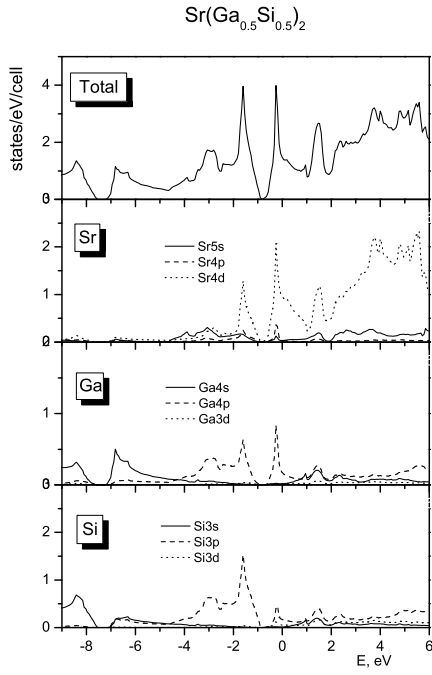


FIG. 6: Total and site-projected  $\ell$ -decomposed DOSs of  $\text{Sr}(\text{Ga}_{0.5}\text{Si}_{0.5})_2$ . The energies are relative to the Fermi level.

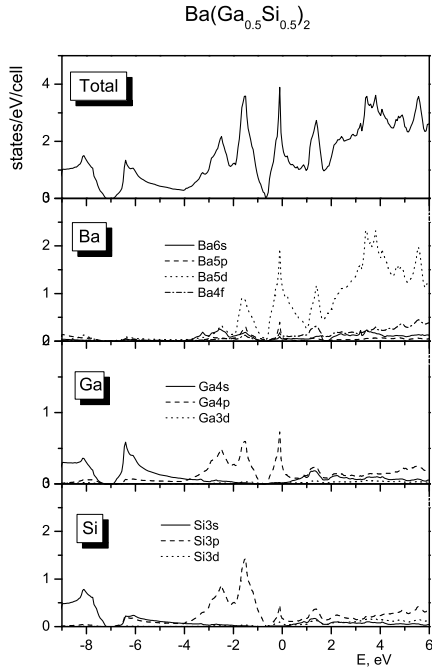


FIG. 7: Total and site-projected  $\ell$ -decomposed DOSs of  $\text{Ba}(\text{Ga}_{0.5}\text{Si}_{0.5})_2$ . The energies are relative to the Fermi level.